High Efficiency Direct Carbon and Hydrogen Fuel Cells for Fossil Fuel Power Generation

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by

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Abstract

Hydrogen fuel cells have been under development for a number of years and are now nearing commercial applications. Direct carbon fuel cells, heretofore, have not reached practical stages of development because of problems in fuel reactivity and cell configuration. The carbon/air fuel cell reaction ($C + O_2 = CO_2$) has the advantage of having a nearly zero entropy change. This allows a theoretical efficiency of 100 % at 700-800 °C. The activities of the C fuel and CO_2 product do not change during consumption of the fuel. Consequently, the EMF is invariant; this raises the possibility of 100% fuel utilization in a single pass. (In contrast, the high-temperature hydrogen fuel cell has a theoretical efficiency of <70%, and changes in fuel activity limit practical utilizations to 75-85%.) A direct carbon fuel cell is currently being developed that utilizes reactive carbon particulates wetted by a molten carbonate electrolyte. Pure CO_2 is evolved at the anode and oxygen from air is consumed at the cathode. Electrochemical data is reported here for the carbon/air cell utilizing carbons derived from fuel oil pyrolysis, purified coal, purified bio-char and petroleum coke. At 800 ° C, a voltage efficiency of 80% was measured at power densities of 0.5-1 kW/m^2. Carbon and hydrogen fuels may be produced simultaneously at high efficiency from: (1) natural gas, by thermal decomposition, (2) petroleum, by coking or pyrolysis of distillates, (3) coal, by sequential hydro-gasification to methane and thermal pyrolysis of the methane, with recycle of the hydrogen, and (4) biomass, similarly by sequential hydrogenation and thermal pyrolysis. Fuel production data may be combined with direct C and H_2 fuel cell operating data for power cycle estimates. Thermal to electric efficiencies indicate 80% HHV [85% LHV] for petroleum, 75.5% HHV [83.4% LHV] for natural gas and 68.3% HHV [70.8% LHV] for lignite coal. Possible benefits of integrated carbon and hydrogen fuel cell power generation cycles are: (1) increased efficiency by a factor of up to 2 over many conventional fossil fuel steam plants, (2) reduced power generation cost, especially for increasing fossil fuel cost, (3) reduced CO_2 emission per kWh, and (4) direct sequestration or reuse (e.g., in enhanced oil or NG recovery) of the CO_2 product.
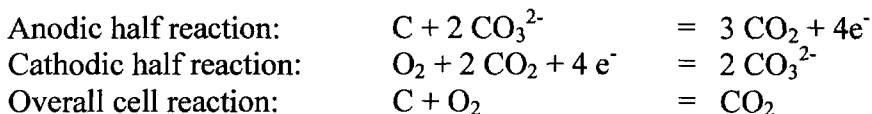
Introduction

Fossil fuels including coal, oil and natural gas make up 85% of the U.S. energy supply and it is projected they will continue to supply this fraction for the next 20 years.[1] Improving efficiency in conversion and utilization of fuel is recognized to be of prime importance in reducing costs to the consumer, reducing polluting emissions, and extending the resource supply.

Generation of electrical power currently consumes about 24% of the total annual fossil fuel supply. Of all power conversion devices, the fuel cell promises maximum conversion efficiency because it can in principle convert the free energy of the combustion reaction into electrical energy. The hydrogen fuel cell has emerged as the leading electrochemical conversion technology for the utilization of fossil fuels. However, generation of hydrogen from fossil fuels is inherently inefficient if hydrogen is the sole fuel used for electricity generation, because of the high carbon content of fossil fuel. To push efficiency to the limit, we propose the decomposition of hydrocarbons derived from fossil fuels into carbon and hydrogen streams. The carbon would be used in a direct carbon conversion cell (DCC) and the hydrogen would be used in an efficient solid oxide fuel cell (SOFC). This sequence enables the conversion of fossil fuels to electricity at efficiencies far in excess of those of conventional fuel cells—in some cases, up to 80% HHV.

The Direct Carbon Fuel Cell

Attempts at directly converting coal to electricity in an electrochemical fuel cell dates to the 19th century.[2] Further attempts were made sporadically during the 20th century with the latest by Weaver of SRI International.[3] The main barriers encountered by these attempts to develop a practical carbon/air fuel cell were: (1) buildup of ash in the molten carbonate electrolyte, (2) low anode reaction rates, and (3) the high cost of carbon electrode manufacture and the logistics of distribution to the cells.

The current approach at LLNL to overcome the historical failures is to employ a low ash, high surface area elemental carbon fuel produced by the low-temperature (<1200 °C) pyrolysis of hydrocarbons derived from the processing of fossil fuels (coal, oil, gas) and biomass. This carbon particulate fuel, once wetted with molten salt, acts like a rigid anode when in contact with an inert metal screen. Turbostratic carbon (i.e., those having a high degree of disorder in the orientation of graphene planes) exhibits unusually high electrochemical reactivity. The anode reaction takes place between the carbon and the carbonate ion from the electrolyte, releasing CO_2 and electrons. At the cathode, oxygen (from air), CO_2 and electrons returning from the anode produce the carbonate ion. A porous ceramic membrane allows the carbonate ion to migrate between the two electrode compartments.

Anodic half reaction:	$C + 2\,CO_3^{2-}$	$= 3\,CO_2 + 4e^-$
Cathodic half reaction:	$O_2 + 2\,CO_2 + 4\,e^-$	$= 2\,CO_3^{2-}$
Overall cell reaction:	$C + O_2$	$= CO_2$

Nickel (with a coating of lithiated nickel oxide) is typically used at the cathode, and the CO_2 for the cathode reaction may be provided by the anodic reaction. The fine particulate carbon may be distributed to the anode compartment by entrainment in a CO_2 stream. A schematic of the components of a typical fuel cell is shown in Figure 1[5].

Features of a Direct Carbon Fuel Cell

The benefit of the fuel cell is that it is not limited by Carnot cycle efficiency. It provides for a direct conversion of chemical to electrical energy to a degree governed by the free energy change of the reaction. The thermodynamic efficiency is the ratio of the free energy of the reaction at the operating temperture T to the standard enthalpy of reaction ($\_G(T)/\_H^{\circ}_{298}$). The free energy change is expressed in terms of enthalpy and entropy changes of the reaction as $\_G = \_H - T\_S$.

For the reaction of carbon and oxygen to form carbon dioxide, the entropy of reaction is positive but nearly zero.[4] As a result, the thermodynamic efficiency is calculated to be 100.3% and is nearly independent of temperature. At 300 K, it is 100.2% at 1000 K it is 100.3%. The standard cell voltage calculated on the basis of the free energy change ($E^{\circ} = -\Delta G(T)/4F$) is 1.03 V for graphite. By comparison the thermodynamic efficiency at 1000 K for a hydrogen/oxygen fuel cell is 70% and for methane (internally reformed to hydrogen in a fuel cell) it is 89% (Table 1).

Another unique feature of the direct carbon cell is that the activity of carbon (a pure substance in its elemental state) is unity and invariant. This allows the possibility of 100% utilization of the carbon fuel in a single pass. Also the CO_2 produced is undiluted and its activity is also invariant. This is not true for gaseous fuels that are continuously diluted with reaction products (for example, H_2, as diluted by H_2O). The utilization efficiency for hydrogen and methane as electrochemical fuels decreases to 75- 85%[2] at practical current densities.

An important feature of the carbon fuel cell is that the reaction product CO_2 is exhausted from the anode compartment as a pure substance. This allows for recovery and disposal or utilization of CO_2 without need for further collection or separation that would add to cost and energy consumption.

Experimental Results

Based on the experimental cell design constructed at LLNL, cell potentials as a function of current density were determined for a number of different types of carbon particulates at a molten salt cell temperature of 800°C, and is shown in Figure 2.[5] The cell power density is a function of the type of carbon fuel. At 0.8 V, current densities in the 60-120 mA/cm^2 range are obtained with the highest current densities for the most "turbostratic" carbons. For the carbon fuels presented in Figure 2, the bio-char have the most disordered crystallographic structure, with deconvoluted domains of crystallinity of ~2.5 nm in the plane of the graphene layers and ~1 nm perpendicular to the graphene layers. The green needle petroleum coke sample, by contrast, has somewhat larger crystallinity domains of ~5 nm by 4 nm, and correspondingly lower reactivity. These results indicate that efficiencies of 80% HHV can be obtained at reasonable power densities for power production. Practical hydrogen powered solid oxide fuel cells operate in the range of 1 kW/m^2 at 0.8 volts[6], which the same as achieved for the most active carbon shown in Figure 2. As in the hydrogen cell, the major loss is due to the oxygen over-voltage at the cathode. Further work (not presented in this paper) with the carbon fuel cell employing state-of-the-art molten carbonate fuel cell cathodes has already shown a reduction in oxygen over-voltage.[7]

The overall efficiency of a fuel cell is the product of 3 terms. Net efficiency = (thermodynamic efficiency) x (fuel utilization factor) x (voltage efficiency). Table 1 compares the net efficiencies of fuel cells for 3 major synthetic or refined fuels. Poor utilization combined with low thermodynamic efficiencies (resulting from entropy reductions in the fuel cell reactions) combine to lower the net efficiency of hydrogen-based systems. Some of these losses may be recovered by bottoming cycles or use of the unreacted fuels elsewhere in the plant, but at an increase in cost and complexity of the system.

Fuel Processing

Since the direct carbon fuel cell depends on an active clean carbon fuel there are basically two constraints for producing a suitable carbon fuel material. First, the carbon must be prepared from abundantly available natural resources. This limits the primary fuels to the fossil fuels, coal, oil, natural gas, and biomass. Secondly, the carbon must be prepared to have a disordered "turbostratic" structure with high surface area and small particulate size (primary particle size less than 100 microns) so that it can be dispersed into molten salt by hydraulic or pneumatic means. The carbon should also have a minimum ash and sulfur content to avoid contaminating the electrolyte and corroding the current collectors. Over the past several decades, a number of processes, some that are industrial and some that have been under development, have the potential of providing the carbon fuel material suitable for direct carbon fuel cells. The major process operations that could yield highly active carbon particulates involve pyrolysis, hydropyrolysis, and thermal decomposition or cracking of natural fossil fuels.

In order to assess the efficiency and energetics and assist in the design of fuel conversion processes, a useful reference table giving the stoichiometric composition and thermodynamics for combustion, heat of formation, and heat of cracking products of the major fossil fuels, biomass and waste materials are given in Table 2. A description of the processes for each type of fuel is given below.[8,9]

Natural Gas

The simplest and cleanest process for obtaining carbon is from the thermal decomposition or cracking of natural gas (methane). Based on the heat of formation of methane, it requires only +18 kcal/mol to crack methane to carbon and hydrogen, as indicated in Table 2. This means that it only takes 8.5% of the heat of combustion of methane (-212.8 kcal/mol) to crack the methane. Cracking processes are about 80% thermally efficient, so that in practice 10.6% of the methane energy is necessary to produce a mol of carbon and 2 moles of hydrogen. For the thermal processes, at pressures below 5 atm and temperatures in the range 800 - 1000°C, thermodynamic equilibrium indicates that 90% of the methane can be dissociated to carbon and hydrogen. Both the carbon and the hydrogen can be used in respective fuel cells for electric power production. There are three industrial processes for production of carbon black, used mainly for reinforcement of automobile tires. The thermal black process uses tandem firebrick furnaces, alternately reheated, and methane is pyrolyzed in the absence of air. The furnace black process partially combusts methane or furnace oil in a rich flame and the carbon fines are collected as product. Both of these processes as currently practiced are very inefficient because energy is not conserved. The hydrogen produced is used as fuel and is not recovered. These processes can be made highly efficient if the hydrogen is used in an integrated power plant. The third and most recently practiced process is the plasma black process that uses an electric discharge to crack the methane. Both the carbon and hydrogen are recovered. The process is claimed to be 90%

efficient. However, electric power consumption reduces the overall fuel efficiency to below 50%, unless a non-fossil fuel source to generate the electricity is used. The industrial plasma black process practiced in Canada (Karbomont, Quebec) uses low cost hydropower.
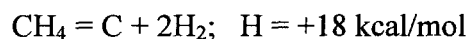
Petroleum

The refining of petroleum for motor fuel (gasoline) and heating oil produces petroleum coke. Petroleum coke is essentially carbon, containing small amounts (less than 1%) of hydrocarbon, ash and sulfur. It is produced by thermal cracking in a "flexicoker" or in a "delayed coker". The hydrogen produced can be used either in the oil refinery to produce gasoline or can be used in fuel cells for power production. Petroleum coke is used in the cement industry as fuel and in the metallurgical industry for aluminum and steel production. The cokers operate at temperatures on the order of $900^\circ C$ and pressures below 5 atm. The carbon from the cokers should be suitable for direct carbon fuel cells. As heavier residual oils are being processed for transportation fuels, the amount of coke being produced is steadily increasing.

Coal

Coal is mainly used to produce electric power and in blast furnaces for steel production. There has been much effort to produce synthetic gaseous and liquid hydrocarbon fuels by gasification and liquefaction processes. Currently there appears to be no industrial process for production of a clean carbon fuel from coals. However, a two-step process has been developed which has potential for producing clean carbon and hydrogen co-products from coal. By hydropyrolysis at high temperature and high pressure ($800 - 900\ ^\circ C$ and $70 - 100$ atm) most of the carbon in coal can be converted to methane.[9] The hydrogenation reaction is also exothermic, thus making the process energy efficient. This is illustrated by the following reaction for lignite coal.

Lignite $CH_{0.8}\ O_{0.22} + 1.82\ H_2 = CH_4 + 0.22\ H_2O + ash;\ \_H = -25$ kcal/mol
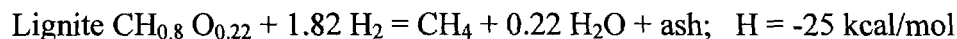
The methane can then be cracked to C and H_2

$CH_4 = C + 2H_2;\ \_H = +18$ kcal/mol

Part of the hydrogen is then recycled to hydrogenate the coal and the remainder becomes a product of the process.

The overall reaction then is

Lignite $CH_{0.8}\ O_{0.22} = C + 0.18\ H_2 + 0.22\ H_2O$
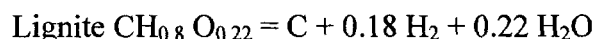
Both the carbon and the hydrogen can be used in fuel cells. Hydropyrolysis has been used experimentally in Germany by the Rheinbraun Co. to generate methane from brown coal. This two-stage reversible hydrogenation process also known as the Hydrocarb process can be used for processing of coal for integrated fuel cell power cycles as shown in Tables 2, 3 and 4.

Biomass

Biomass as a prime renewable energy resource in the form of wood, agricultural products and municipal solid waste can be processed to produce carbon and hydrogen for fuel cell power generators. The hydrogenation of wood (followed by methane pyrolysis in a manner similar to that described above for coal) can be used to generate the carbon and hydrogen.

The hydrogenation takes place at a temperature of 800°C to 900°C and pressures of about 70 atm. The reactivity of biomass is higher than that of coal so that the condition for processing wood is less severe than for coal. Furthermore, the ash content of wood ($\sim$ 1%) is much lower than that from coal.

The process reactions are as follows:

Wood hydrogenation:　$CH_{1.44} O_{0.66} + 2H_2 = CH_4 + 0.06 H_2 + 0.66 H_2O$
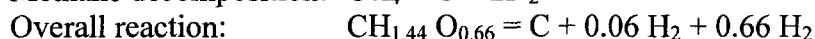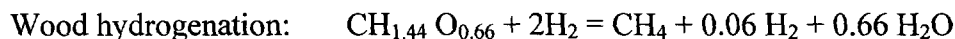Methane decomposition:　$CH_4 = C + 2H_2$
Overall reaction:　$CH_{1.44} O_{0.66} = C + 0.06 H_2 + 0.66 H_2$

High Efficiency Power Generation Cycles

The high efficiency direct carbon fuel cell (DCC) and the solid oxide hydrogen fuel cell (SOFC) integrated with fuel processing to carbon and hydrogen in a combined cycle and using a back-end Rankine steam plant, maximizes the power generation efficiently.[8,9] Figure 3 shows a schematic of the components for a natural gas integrated fuel cells, combined cycle power plant. The hot H_2O and CO_2 effluents from the fuel cells are used in a back-end steam cycle. For natural gas, only a thermal decomposition reactor is needed for fuel processing.

Figure 4 shows the power plant schematic for a coal (lignite) fuel In this case a two-reactor system, a hydropyrolyzer and a methane decomposer is needed for fuel processing.

Figure 5 shows the power plant schematic for petroleum fuel. A coker is used to produce carbon and the hydrogen is returned to the refinery for producing liquid hydrocarbon fuels. Figure 6 shows petroleum fuel in an integrated fuel cell combined cycle plant, which makes use of both the carbon and the hydrogen from the coker in fuel cells.

Figure 7 shows a power plant schematic using biomass (wood) as fuel. In this case a hydropyrolyzer followed by a methane decomposer are used to process the wood. Since very little excess H_2 is produced, only the carbon is used in the fuel cell for power production. The hot CO_2 effluent gas is used to make up the heat balance of the process instead of a back-end steam plant.

Table 3 lists a summary of the selected unit process parameters for processing the fossil fuel resources to produce elemental carbon and hydrogen for integration with fuel cells and a combined cycle for electric power generation.[8,9] The distribution of power generation, the unit thermal efficiency and the overall power plant efficiency are calculated and given in the table for each unit. The efficiencies are based on achievable values for carbon and hydrogen fuel cells. The overall power plant efficiency is calculated by summing the enthalpy of conversion of each of the units and dividing by the enthalpy of combustion of the fuel. Both lower (LHV) and higher (HHV) heating values are given. The highest efficiency is obtained with petroleum coke,

followed by natural gas, lesser with coal and lowest with biomass. However, all overall efficiencies are well above 60%--nearly twice as high as many conventional power plants.

Economic and Environmental Assessment of Integrated Direct Carbon Fuel Cell Plants

Based on current costs of fossil fuels and estimates of unit capital investment of fuel cells and conventional power plants, estimates of the cost of power generation for each of the integrated fuel cell plants and for typical current and advanced conventional plants are made. The unit CO_2 emissions are calculated for each power cycle, which is a measure of its impact on the environment. The cost assumptions include a fixed charge of 20% on capital investment taking into account depreciation and taxes and a 15% charge for operation and maintenance of the fixed charge amount.[8,9] Table 4 gives a summary comparison of the economic and environmental parameters for the fuel cell plants with conventional coal and gas plants. The coal integrated carbon fuel cell (ICFC) plant is 80% more efficient than a conventional Rankine pulverized coal (PV) steam plant and 37% more efficient than a combined cycle gasification plant. At $1/MMBTU, the lignite ICFC plant yields the lowest electricity production cost even when the unit capital cost is about the same for all three of these plants. A conservative $900/kw(e) has been estimated for the carbon fuel cell. The projected cost may be as low as $500/kw(e) which would result in a much lower production cost estimate for ICFC. The CO_2 emissions for an ICFC plant are a significant 44% lower than a PV steam plant. Furthermore, the CO_2 effluent is undiluted and ready for sequestration or utilization without further separation.

The natural gas fired ICFC plant is over 90% more efficient than a conventional natural gas fired plant. The ICFC is also 26% more efficient than the current most efficient NG combined cycle plant, which currently reaches 60%. The cost of natural gas has been very volatile over the last year. The historical cost has been $2/MMBTU. It has gone up as high as $10/MMBTU and has recently decreased to a little over $3/MMBTU. Table 4 shows that at $2/MMBTU and at $4/MMBTU the ICFC plant would produce electricity at a slightly higher cost than the NGCC plants available today but at a lower cost than a conventional natural gas fired steam plant. However, at higher $6/MMBTU for natural gas, the ICFC plant becomes more economical. In any case, the CO_2 emission is reduced by 47% and 73% lower than conventional gas or coal fired plants, respectively. In terms of the cost of obtaining CO_2 removal and sequestering CO_2 at $4/MMBTU, the cost of reduction of CO_2 amounts to $23/ton CO_2 which is 2 to 3 times lower than estimates for removal and disposal of CO_2 from conventional plants. Furthermore, the CO_2 from ICFC is undiluted and can be sequestered or utilized directly requiring no further separation cost.

For oil fired power plants, the ICFC plant is over 110% more efficient than a conventional steam plant. Using petroleum coke, based on carbon alone, the efficiency is 140% more efficient. However, based on the total barrel of oil it is only 50% more efficient, because the hydrogen is used in producing liquid fuels in the refinery. Oil costs have also been volatile over the last year but at $25/bbl oil, the cost of electricity from an ICFC plant is 33% lower than an oil fired steam plant. The CO_2 reduction is 52% lower than a conventional oil fired plant and as much as 64% lower than a conventional PV coal fired steam plant.

Conclusion

In conclusion, more efficient fossil fuel ICFC plants can generate electric power more economically (10- 33% lower than conventional steam plants), and can significantly reduce CO_2

emissions by 44-73%. In the case of biomass as a fuel, the CO_2 reduction is 100% and assuming biomass can be obtained for \$2/MMBTU the cost of power can be about 13% lower than a conventional steam plant. The direct carbon fuel cell provides the following advantages: (1) a significant increase in thermal efficiency of combined cycle direct carbon fuel cell power plants, (2) a significant decrease in CO_2 emissions, (3) a pure CO_2 stream which can be directly sequestered or utilized, and (4) a lower production cost than conventional plants. There is thus ample motivation for continuing the research and development of a direct carbon fuel cell including the fuel processing necessary for producing an electrochemically reactive carbon fuel. The integrated carbon fuel cell plants can be used in distributed as well as central power plant stations.

References

1. U.S. Energy Association, Towards a Natural Energy Strategy, Washington, D.C. (February 2001).

2. Liebhafsky, H.A. and Cairns, E.D., Fuel Cells and Batteries, (John Wiley and Sons, N.Y. 1968).

3. Weaver, R.D., Leach, S.C., Bayer, A.E., and Nanis, L., Direct Electrochemical Generation of Electricity from Coal Report, May 16, 1977-Feb. 15, 1979; SRI International, Menlo Park, CA 94025 (NTIS Report SAN-0115-1) and Weaver, R.D. and Navis, L., "Electrochemical Oxidation of Carbon in Molten Carbonate Coal-air Fuel Cell, Proc. 3rd International Symposium on Molten Salts, Electrochem. Soc. Vol. 81-9, p. 316 (1981); see also Vutetakis, D. G.; Skidmore, D. R.; Byker, H. J.; Electrochemical oxidation of molten salt carbonate-coal slurries, J. Electrochem. Soc. v 134 (12) Dec 1987 p 3027-3035.

4. JANAF Thermochemical Tables, Second Edition, NSRD-NBS37 Superintendent of Documents, Washington, DC, 20402 (1971).

5. Cooper, J. F., Cherepy, N., Berry, G., Pasternak, A., Surles, T., and Steinberg, M. "Direct carbon conversion applications to the efficient conversion of fossil fuels, (Global Climate Change: a Coordinated response by Electrochemistry and Solid-State Science and Technology, ed. A. Wieckowski, Proc. First International Symposium, Vol.2000-20, p. 78, The Electrochemical Society, April 2001.); see also, "Turning carbon directly into electricity," cover article, Science and Technology Review, Lawrence Livermore National Laboratory, June 2001.

6. Fuel Cell Handbook, 4th Edition, U.S. Dept. of Energy Office of Fossil Fuel, Federal Energy Technology Center, Morgantown, WV, DOE FETC-99/1076 (1999).

7. Cherepy, N.J., Cooper, J.F., "Direct Conversion of Carbon Fuels in a Molten Carbonate Fuel Cell," J. Electrochem. Soc., in preparation.

8. Steinberg, M., Technologies and Economics for Production of Electrochemical Fuels from Fossil Fuel Resources for Use in High Efficiency Integrated Fuel Cell Combined Cycle Power Generation Plants, Internal Report, Lawrence Livermore National Laboratory, Livermore, CA (May 2001).

9. Steinberg, M., Additional Processes for Producing Clean Carbon Fuel for Use in the Carbon Fuel Cell, Internal Report to Lawrence Livermore National Laboratory, Livermore, CA (July 2001); to be published.

Electric power out

− +

Air in

Carbon in
Reactive, nano-scale
disorder C from thermal
decomposition of CH_x

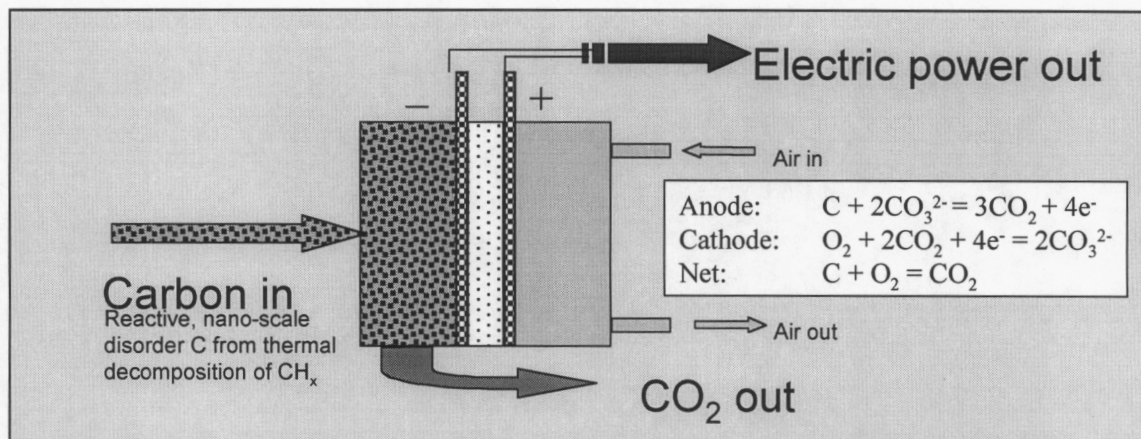| Anode:	$C + 2CO_3^{2-} = 3CO_2 + 4e^-$
Cathode:	$O_2 + 2CO_2 + 4e^- = 2CO_3^{2-}$
Net:	$C + O_2 = CO_2$

Air out

CO_2 out

Figure 1. In Direct Carbon Conversion (DCC), electric power is generated from the electrochemical reaction of carbon and atmospheric oxygen, using a fuel cell will a molten carbonate salt electrolyte at 750-800 °C.
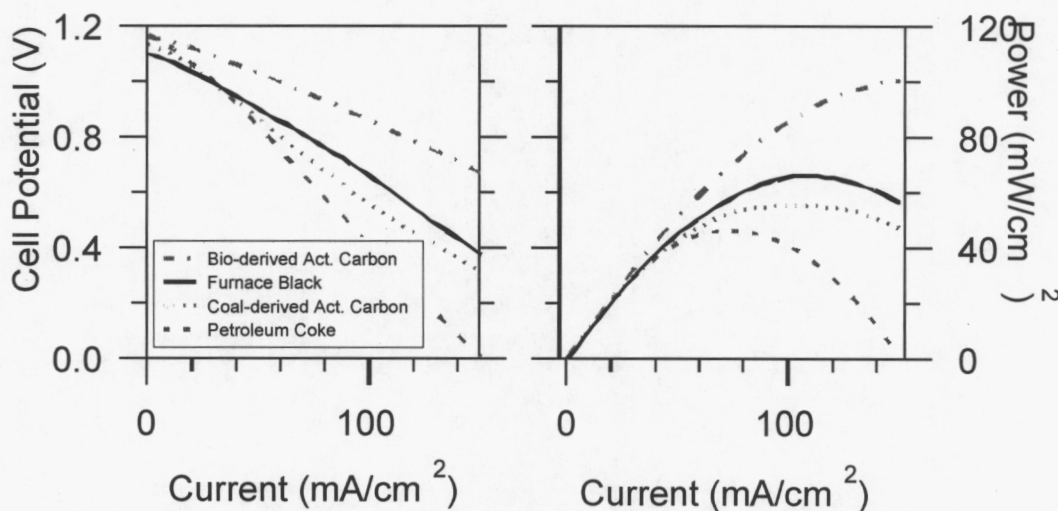
Figure 2. Conversion efficiency of 80% has been demonstrated at 0.8 V and 100 mA/cm² in carbon/air cells using carbon derived from biomass. For common fuels (derived from furnace oil, coal and green petroleum coke), peak power densities have been achieved in the range 50-70 mW/cm². More recent work indicates that that power may be doubled with an improved air cathode, moving the power density for DCC into the 100 mW/cm² range for furnace blacks and petroleum cokes and to nearly 200 mW/cm² for biomass-derived carbons. Open circuit potentials differ from the standard cell potential of 1.03 V because of non-standard gas composition adjacent to the anode and cathode.

Power DC to AC
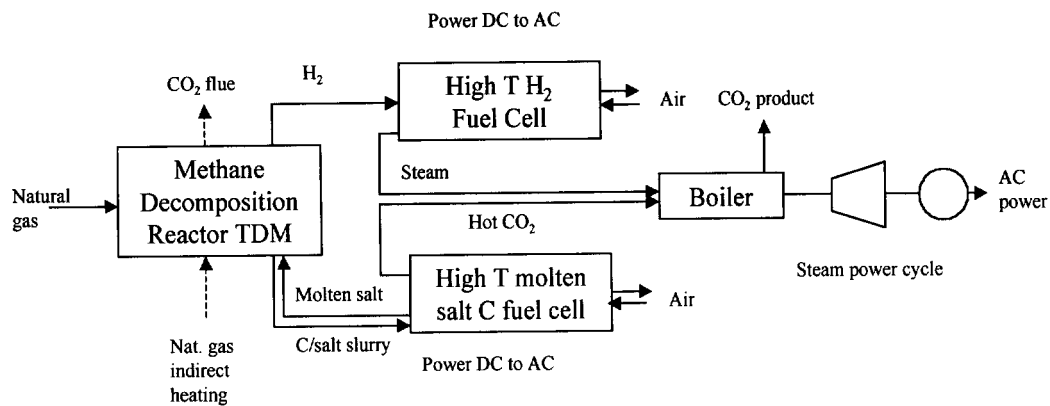
Potential overall thermal efficiency = 75.5% HHV NG [83.4% LHV NG]

Figure 3. Flow diagram is shown for a natural gas fuel cell power cycle.

$CH_{0.8}O_{0.22} = C + 0.18\ H_2 + 0.22\ H_2O$
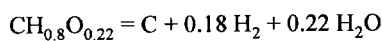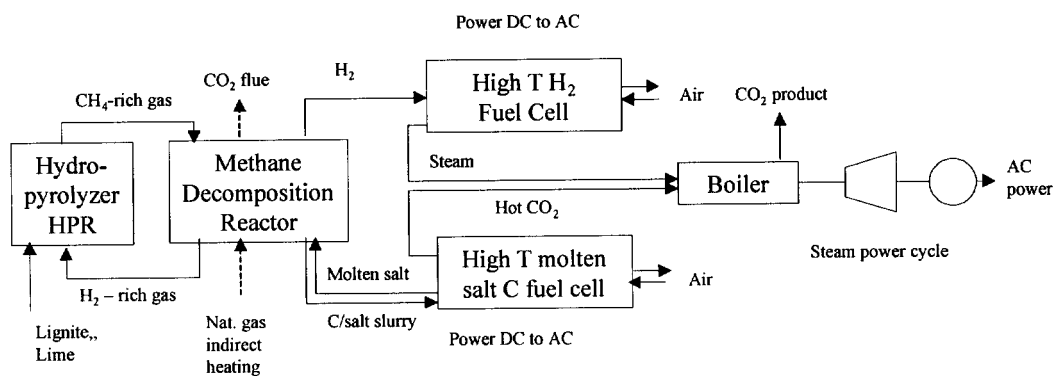
Potential overall thermal efficiency = 68.3% HHV coal [70.8 % LH V coal]

Figure 4. Flow diagram for coal fueled reversible "Hydrocarb" combined fuel cell power cycle.
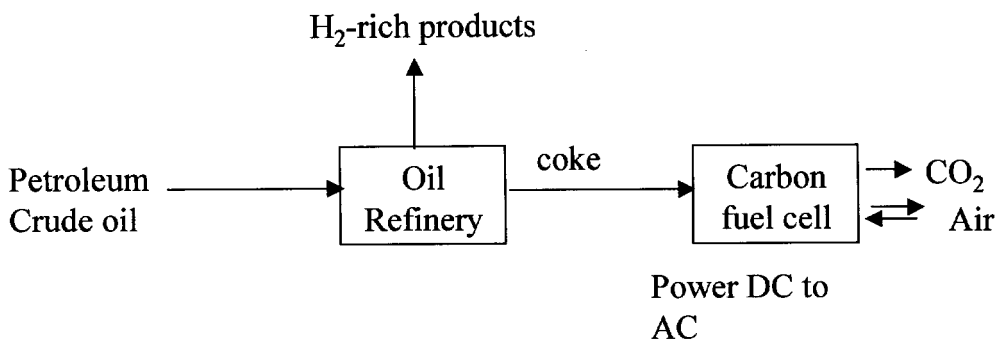
Figure 5. Flow diagram for use of petroleum coke byproducts of petroleum refining.

Hydro-pyrolyzer: $CH_{1.44}O_{0.66} + 2H_2 = CH_4 + 0.06H_2 + 0.66H_2O$
Methane decomposition: $CH_4 = C + 2H_2$
Overall reaction: $CH_{1.44}O_{0.66} = C + 0.06H_2 + 0.66H_2O$
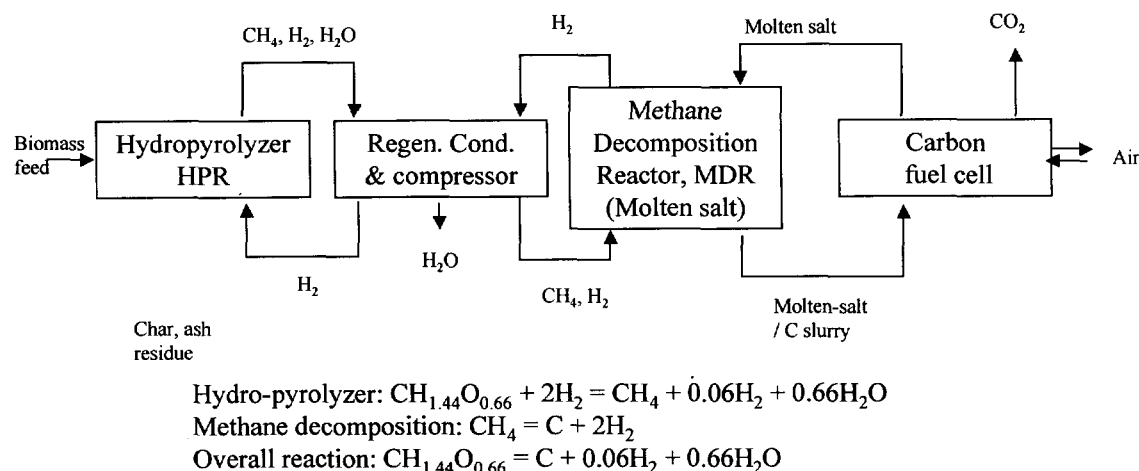
Figure 6. Crude oil fired integrated combined fuel cell power cycle.

$CH_{1.7} = C + 0.85 H_2$
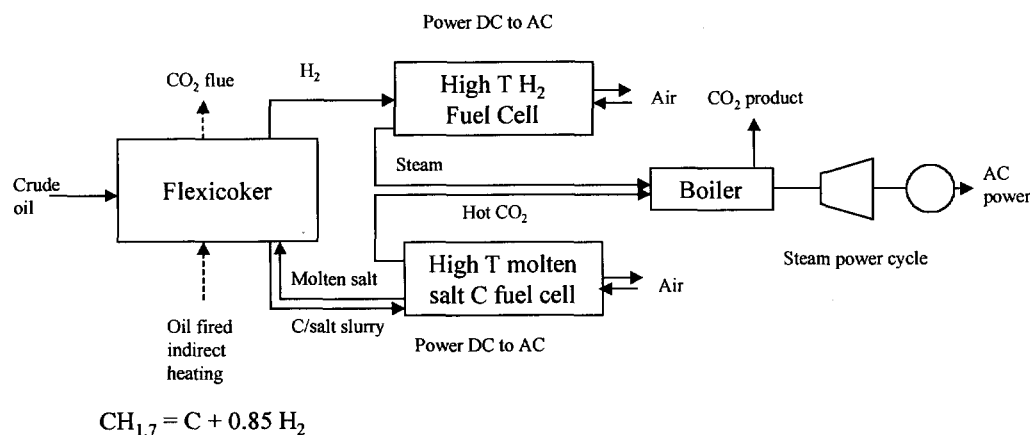
Potential overall thermal efficiency = 80% HHV crude oil [85 % LHV crude oil]

Figure 7. Biomass fueled carbon fuel cell power plant.

Table 1.

Comparison of Efficiencies of Fuel Cells Using Synthetic or Refined Fuels, T = 750-850 °C

Fuels	Thermal efficiency $\Delta G°(T)/\Delta H°_{298}$	Fuel utilization factor	Voltage Efficiency**	Net efficiency
C	100.3	1.0	0.8-0.9	0.80-0.90
H_2	70	0.75-0.85	0.8	0.42-0.48
CH_4*	89	0.75-0.85	0.8	0.53-0.60

*Assumes efficient internal steam reforming reaction.
**Referenced to equilibrium cell voltage at operating temperature, T.

Table 2
Thermodynamics of Various Carbonaceous Feedstock

Feedstock	Stoichiometric Formula[1]	Heat of Combustion[2] (Kcal/Mole)		Heat of Formation[2] (Kcal/Mole)	Heat of Cracking[2] Cracking Products	(Kcal/Mole)
		HHV	LHV			
Natural Gas	CH_4	-212	192	-18	$C(s) + 2H_{2(g)}$	+18
Petroleum Medium Crude Resids, Tar, Sands, Shale	$CH_{1.7}$	-149	141	-3	$C(s) + 0.85H_{2(g)}$	+3
Wood (Biomass)						
Sawdust	$CH_{1.44}O_{0.66}$	-105	98	-38	$C(s) + 0.06H_{2(g)} + 0.66H_2O_{(P)}$	-7
Pine (12% Moisture) MSW and Paper Waste	$CH_{1.44}O_{0.66}$	-127	120	-16	$C(s) + 0.06H_{2(g)} + 0.66H_2O_{(P)}$	-29
Rubber Styrene-Butadiene (Synthetic)	$CH_{1.15}$	-142	136	+9	$C(s) + 0.58H_{2(g)}$	-9
Natural Rubber (Isoprene) Industrial Waste	$CH_{1.6}$	-144	136	-5	$C(s) + 0.8H_{2(g)}$	+5
Coal						
Bituminous	$CH_{0.8}O_{0.08}$	-116	112	-5	$C(s) + 0.32H_{2(g)} + 0.08H_2O_{(P)}$	-1
Lignite	$CH_{0.8}O_{0.22}$	-113	109	-8	$C(s) + 0.18H_{2(g)} + 0.22H_2O_{(P)}$	-7

(1) Representative formulae, based on a single atom of carbon in feedstock. Specific samples will vary in composition.
(2) All heats of combustion, formation, and cracking (at 298.2°K) are based upon one gram mole of feedstock containing one gram atom of carbon – HHV represents higher heating value and LHV is lower heating value.

Table 3
**Summary of Process Parameters for Integrated Carbon and Hydrogen
Fuel Cell Combined Cycle Power Plants**

Process Unit	Unit Conditions		Unit Thermal Efficiency %	% Contribution of Unit to Power Plant Capacity
	Pressure	Temperature		
Natural Gas Fired				
1) Methane Decompoition Thermal Black Reactor	1-5 atm	800-1000°C	80% Proc. Efficiency	-
2) C/Air Fuel Cell Molten Salt Electrolyte	1-5 atm	750-1000°C	90%	45.3%
3) H_2/Air Fuel Cell High Temp. SOFC	1-5 atm	1000°C	55.6%	40.5%
4) Boiler and Steam Turbine Rankine Cycle	70 atm	600°C	<u>38.0%</u>	<u>14.2%</u>
	Overall Power Plant Efficiency		75.5% HHV 83.4% LHV	100.%
Coal Fuel				
1) Hydropyrolyzer Fluidized Bed Reactor	70 atm	800-900°C	90% Conversion Eff.	-
2) Methane Decomposition Thermal Black Reactor	1-5 atm	900-110°C	80% Proc. Efficiency	-
3) C-Fuel Molten Salt Electrolyte	1-5 atm	750-1000°C	90%	86.3%
4) High Temp. H_2 Fuel Cell Solid Oxide Electrolyt	5 atm	1000°C	55.6%	7.7%
5) Boiler and Steam Turbine Rankine Cycle	70 atm	600°C	38.0%	6.0%
	Overall Power Plant Efficiency		68.3% HHV 70.8% LHV	100.%
Petroleum Fuel				
1) Coker	1-5 atm	800°C	80% Proc.	-
2) C-Fuel Cell Molten Salt Electrolyte	1-5 atm	750°C-1000°C	90%	65.1%
3) High Temp. H_2 Fuel Cell Solid Oxide Electrolyte	1-5 atm	1000°C	55.6%	24.7%
4) Boiler and Steam Turbine Rankine Cycle	70 atm	600 °C	38%	10.2%
	Overall Power Plant Efficiency		80.0% (HHV) 85.0% (LHV)	100%
Biomass (Wood) Fuel				
1) Hydropyrolyzer (HPR) Fluidized Bed Reactor		800°-900°C	90% Conversion Eff.	-
2) Methane Decomposition Reactor Slurry Contacter	1-5 atm	900°-1000°C	80% Proc. Efficiency	-
3) C-Fuel Cell Molten Salt Electrolyte	1-5 atm	750°-1000°C	90%	100%
	Overall Power Plant Efficiency		64.4% (HHV) 68.8% (LHV)	100%

Table 4
Summary Comparison of Economic and Environmental Parameters for Integrated Carbon Fuel Cell Power Plants with Conventional Plants

Plant Type	Thermal Eff.% (HHV)	(LHV)	Cap Cost $/Kw	Electricity Production Cost Mills/Kwh(e)			Net CO_2 Emission $LbCO_2$/Kwh(e)	% Reduction from Conventional plant type
Coal Fired				$1/MMBTU				
*Rankine Steam Cycle Conventional (PV)	38%	39.4%	$1300	52.8			1.943*	0
Integrated Gasification Combine Cycle (IGCC)	50%	51.8%	$1300	50.4			1.476	24%
Integrated Carbon Fuel Cell Combined Cycle (ICFCC)	68.3%	70.8%	$1300	48.3			1.080	44%
Natural Gas Fired				$2/MMBTU	$4/MMBTU	$6/MBTU		
Rankine Steam Cycle Conventional (NG)	38%	44.2%	$600	37.7	55.7	73.7	0.980	0
Combined Cycle (NGCC)	60%	66.2%	$700	34.4	45.8	57.1	0.653	33%
Integrated Carbon Fuel Cell Combined Cycle (ICFCC)	75.5%	83.4%	$900	38.6	47.7	56.7	0.519*	47%
*ICFCC CO_2 Reduction from Conventional Coal Fired Plant						=		73%
Oil Fired				$25/Bbl Oil				
Rankine Steam Conventional Cycle (P)	38%	40%	$900	79.4			1.470	0
Integrated Carbon Fuel Cell Combined Cycle (ICFCC)	80%	85%	$900	53.2			0.700*	52.4%
Petroleum on C Coke (PC) for oil	90% 55.8%	90% 59.3%	$900	50.2			0.986	33.0%
*ICFCC CO_2 Reduction from Conventional Coal Fired Plant						=		64.0%
Biomass Fuel				$2/MMBT				
Rankine Steam Conventional Cycle	38.0%	40.7	$1200	57.4			0	0
Integrated Gasification Combined Cycle (IGCC)	50.0	53.5	$1200	53.1			0	-
Integrated Carbon Fuel Cell Combined Cycle (ICFCC)	64.4	68.8	$1200	50.0			0*	-
*ICFCC CO_2 Reduction from Conventional Coal Fired Plant						=		100.0%